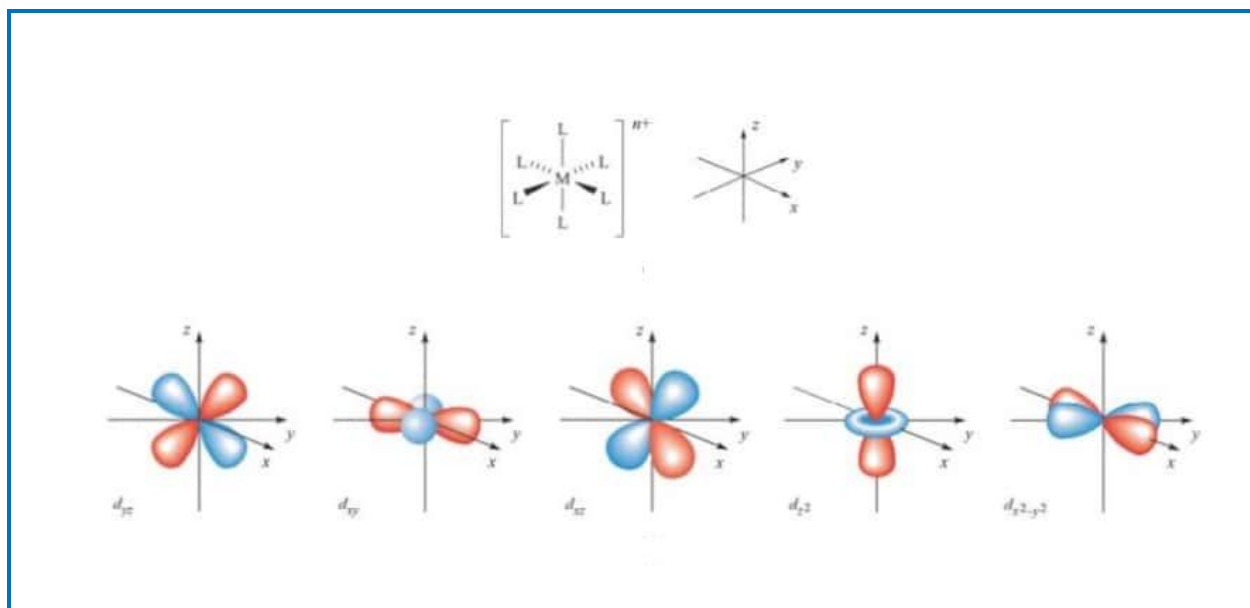


## CEMG-CC4/GE4

### CRYSTAL FIELD THEORY (CFT):

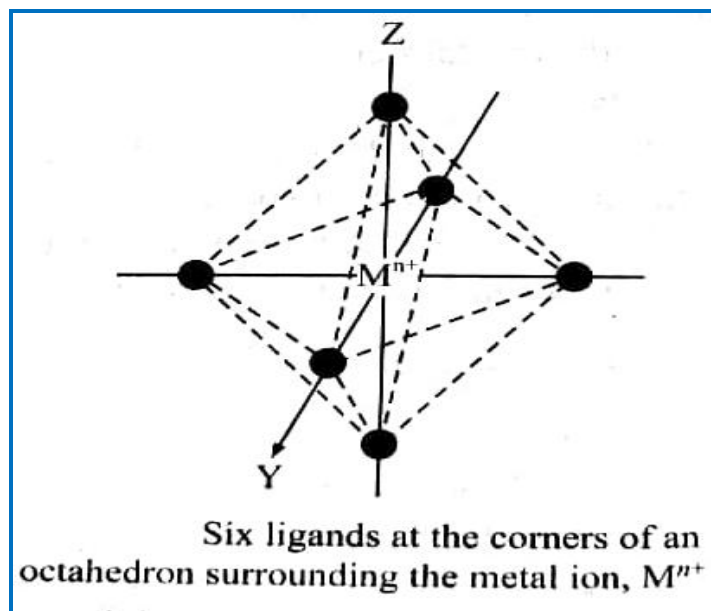
The crystal field theory (CFT) is an electrostatic model which considers the metal-ligand bond to be ionic arising purely from electrostatic interactions between the **metal ion and the ligand**. Ligands are treated as **point charges in case of anions (F<sup>-</sup>, Cl<sup>-</sup>, CN<sup>-</sup>)** or **dipoles in case of neutral molecules (H<sub>2</sub>O, NH<sub>3</sub>, CO)**. The five 'd' orbitals in an isolated gaseous metal atom/ion have **same energy, i.e., they are degenerate**. This degeneracy is maintained if a spherically symmetrical field of negative charges surrounds the metal atom/ion. However, when this negative field is due to ligands (either anions or the negative ends of dipolar molecules) in a complex, it becomes asymmetrical and the degeneracy of the d orbitals is lifted. It results in splitting of the d orbitals. The pattern of splitting depends upon the nature of the crystal field.

In order to understand clearly the interactions that are responsible for crystal or ligand field effects in transition metal complexes, it is necessary to know the geometrical relationships of **the 'd' orbitals**. There are five wave functions that can be written for orbitals having the typical four-lobed form.



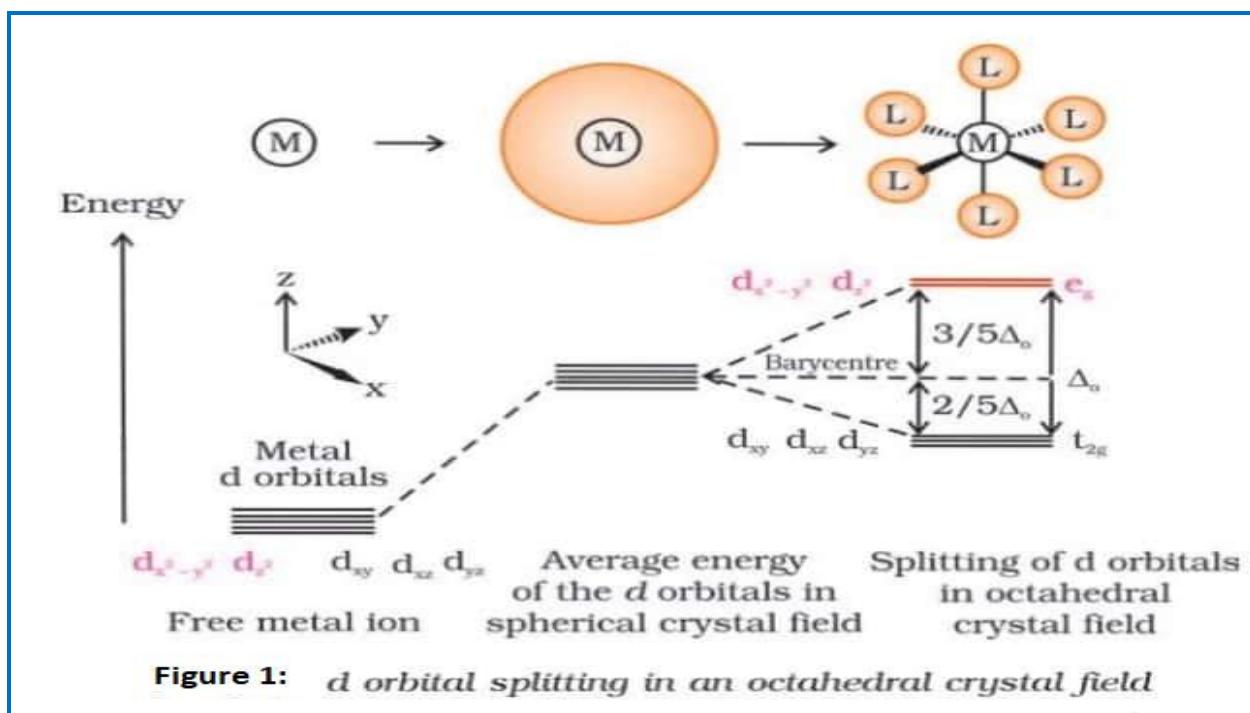
### Crystal Field Effects in Octahedral ( $O_h$ ) Complexes

In case of **free metal ion** all the five d-orbitals are degenerate (these have the same energy). Now consider an octahedral complex,  $[ML_6]^{n+}$  in which the **central metal cation,  $M^{n+}$**  is placed at the center of the octahedron and is **surrounded by six ligands** which reside at the six corners of the octahedron.



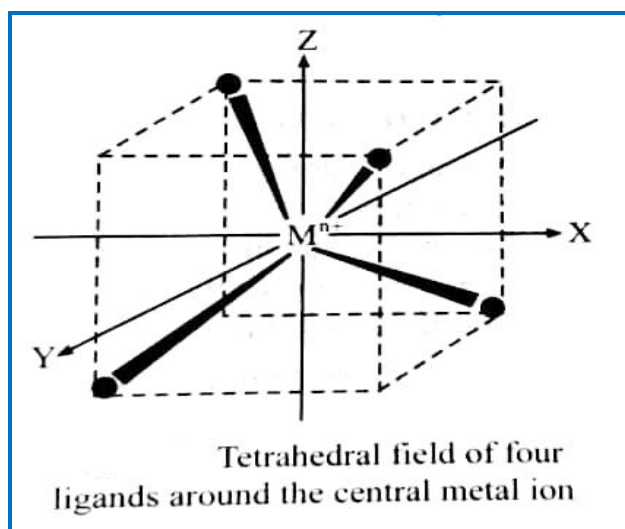
Now suppose both the ligands on each of the three axes are allowed to approach towards the metal cation,  $M^{n+}$  from both the ends of the axes. In this process the electrons in d-orbitals of the metal cation are repelled by the negative point charge or by the negative end of the dipole of the ligands. This repulsion will raise the energy of all the five d-orbitals. Since the lobes of  $d_{z^2}$  and  $d_{x^2-y^2}$  orbitals ( $e_g$  orbitals) lie directly in the path of the approaching ligands, the electrons in these orbitals experience greater force of repulsion than those in  $d_{xy}$ ,  $d_{yz}$ , and  $d_{zx}$  orbitals ( $t_{2g}$  orbitals) whose lobes are directed in space between the path of the approaching ligands (the energy of  $e_g$  orbitals is increased while that of  $t_{2g}$  is decreased (greater the repulsion, greater the increase in energy)).

Thus we find that under the influence of approaching ligands, the five d-orbitals which were originally degenerate in free metallic cation are now split (or resolved) into two levels,  $t_{2g}$  level which is triply degenerate and is of lower energy, and  $e_g$  level which is doubly degenerate and is of higher energy. This splitting of the degenerate levels due to the presence of ligands in a definite geometry is termed as crystal field splitting and the energy separation is denoted by  $\Delta_o$  ('o' for octahedral; OR the term  $10Dq$  instead of  $\Delta_o$ ) (Figure 1). Thus, the energy of the two  $e_g$  orbitals will increase by  $(3/5) \Delta_o$  and that of the three  $t_{2g}$  will decrease by  $(2/5) \Delta_o$ .



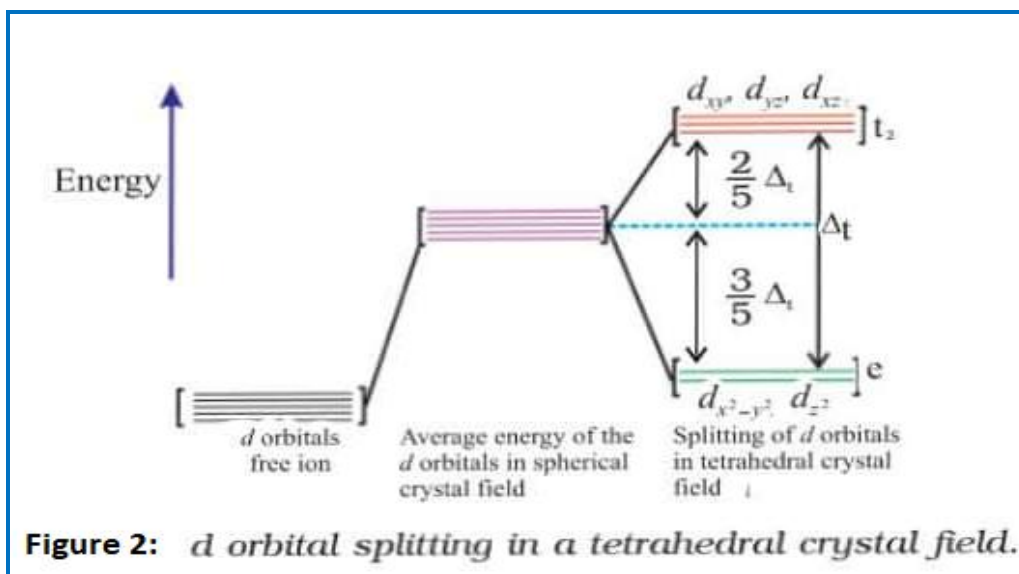
### Crytal Field Effect in Tetrahedral ( $T_d$ ) Complexes

Let us consider a tetrahedral complex ion,  $[ML_4]^{n+}$  in which the central metal ion ( $M^{n+}$ ) is surrounded by **four ligands**.



A tetrahedron may be supposed to have been formed from a cube. The center of the cube is the center of the tetrahedron at which is placed the central metal ion ( $M^{n+}$ ). Four alternate corners of the cube are the four corners of the tetrahedron at which the four ligands, L are placed. The four ligands are lying between the three axes x,y and z which pass through the centers of the six faces of the cube and thus go through the center of the cube. Now since the lobes of  **$t_2$  orbitals** ( $d_{xy}$ ,  $d_{yz}$  and  $d_{zx}$ ) are lying between the axes (are lying directly in the path of the ligands), these orbitals will experience greater force of

repulsion from the ligands than those of **e orbitals** ( $d_z^2$  and  $d_{x^2-y^2}$ ) whose lobes are lying along axes (are lying in space between the ligands). Thus the energy of  **$t_2$  orbitals** will be increased while that of **e orbitals** will be decreased. Consequently the d orbitals are split into two sets (figure 2).



The energy difference between  $t_2$  and e sets for tetrahedral complex is represented as  $\Delta_t$ . The crystal field splitting in a tetrahedral field is smaller than that in an octahedral field because in an octahedral complex there is a ligand along each axis and in a tetrahedral complex no ligand lies directly along any axis. For this reason and also because there are only four ligands in the tetrahedral complex, while in an octahedral complex there are six ligands, the **tetrahedral orbital splitting,  $\Delta_t$  is less than  $\Delta_o$**  for the same metal ion, ligands and metal-ligand distances,

$$\Delta_t = \frac{4}{9} \Delta_o .$$

*All the tetrahedral complexes are high spin complexes.*

### Crystal Field Stabilization Energy (CFSE)

The amount of stabilization provided by splitting of the d-orbitals into two levels is called crystal field stabilization energy (CFSE).

Thus, in octahedral field for each electron that enters the  **$t_{2g}$  orbital**, the crystal field stabilization energy is  **$-0.4\Delta_o$  ( or  $-4 D_q$ )** and for each electron that enters the  **$e_g$  orbital** the crystal field stabilization energy is  **$+0.6\Delta_o$  (or  $+6 D_q$ )** (as,  $\Delta_o = 10 D_q$ ).

### CFSE for various Octahedral ( $O_h$ ) Complexes:

(i) For a  $d^1$  system (e.g.  $Ti^{3+}$  ion):

The electronic configuration is  $t_{2g}^1$

$$\text{CFSE} = 1 \times (-0.4\Delta_o) = -0.4\Delta_o$$

(ii) For  $d^2$  system (e.g.  $V^{3+}$  ion):

The electronic configuration is  $t_{2g}^2$

$$\text{CFSE} = 2 \times (-0.4\Delta_o) = -0.8\Delta_o$$

(iii) For  $d^3$  system (e.g.  $Cr^{3+}$  ion):

The electronic configuration is  $t_{2g}^3$

$$\text{CFSE} = 3 \times (-0.4\Delta_o) = -1.2\Delta_o$$

When one more is added to form the  $d^4$  case, two possibilities arise: **either the electron may enter the higher energy  $e_g$  level or it may pair with another electron in one of the  $t_{2g}$  orbitals**. The actual configuration adopted will, of course, be the lowest energy one and will depend on the relative magnitudes of  $\Delta_o$  and  $P$ , pairing energy.

(a) For  **$\Delta_o < P$  (the weak field or high spin condition)**, the fourth electron will enter one of the  $e_g$  orbitals rather than of pairing with one in a  $t_{2g}$  orbital. The configuration will be  $t_{2g}^3 e_g^1$  and the net CFSE will be

$$\text{CFSE} = (3 \times -0.4 \Delta_o) + (1 \times +0.6 \Delta_o) = -0.6 \Delta_o$$

The addition of a fifth electron to a weak field complex gives a configuration  $t_{2g}^3 e_g^2$  and a CFSE of zero.

(b) If the splitting of d orbitals is large with respect to the pairing energy ( **$\Delta_o > P$** ), it is more favorable for electrons to pair in the  $t_{2g}$  level than to enter the strongly unfavorable  $e_g$  level. In these **strong field or low spin complexes**, the  $e_g$  level remains unoccupied for  $d^1$  through  $d^6$  ions.

Thus, for a  $d^4$  system, there are two possibilities:

(i)  **$d^4$  low spin complex (strong field)** having  $t_{2g}^4$  configuration,  $\text{CFSE} = 4 \times (-0.4\Delta_o) + P = -1.6\Delta_o + P$

Where,  $P$  = pairing energy

(ii)  **$d^4$  high spin complex (weak field)** having  $t_{2g}^3 e_g^1$  configuration,  $\text{CFSE} = 3 \times (-0.4\Delta_o) + 1 \times 0.6\Delta_o = -0.6\Delta_o$

For  $d^5$  system:

(i) **Strong field:**  $t_{2g}^5$  configuration

$$\text{CFSE} = 5 \times (-0.4\Delta_o) + 2P = -2.0\Delta_o + 2P$$

(ii) **Weak field:**  $t_{2g}^3 e_g^2$  configuration

$$\text{CFSE} = 3 \times (-0.4\Delta_o) + 2 \times 0.6\Delta_o = 0$$

**Crystal field stabilization energies for metal ions having different numbers of  $d$ -electrons in octahedral complexes.**  
(Values for weak and strong fields are given separately where applicable)

| Number of electrons | Weak field | CFSE                              | Strong field | CFSE                                        |
|---------------------|------------|-----------------------------------|--------------|---------------------------------------------|
| $d^1$               |            | $-4 Dq$<br>or<br>$-0.4 \Delta_0$  |              |                                             |
| $d^2$               |            | $-8 Dq$<br>or<br>$-0.8 \Delta_0$  |              |                                             |
| $d^3$               |            | $-12 Dq$<br>or<br>$-1.2 \Delta_0$ |              |                                             |
| $d^4$               |            | $-6 Dq$<br>or<br>$-0.6 \Delta_0$  |              | $-16 Dq + P$<br>or<br>$-1.6 \Delta_0 + P$   |
| $d^5$               |            | 0                                 |              | $-20 Dq + 2P$<br>or<br>$-2.0 \Delta_0 + 2P$ |
| $d^6$               |            | $-4 Dq$<br>or<br>$-0.4 \Delta_0$  |              | $-24 Dq + 2P$<br>or<br>$-2.4 \Delta_0 + 2P$ |
| $d^7$               |            | $-8 Dq$<br>or<br>$-0.8 \Delta_0$  |              | $-18 Dq + P$<br>or<br>$-1.8 \Delta_0 + P$   |
| $d^8$               |            | $-12 Dq$<br>or<br>$-1.2 \Delta_0$ |              | $-12 Dq$<br>or<br>$-1.2 \Delta_0$           |
| $d^9$               |            | $-6 Dq$<br>or<br>$-0.6 \Delta_0$  |              |                                             |
| $d^{10}$            |            | 0                                 |              |                                             |

## CFSE for various Tetrahedral ( $T_d$ ) Complexes:

Energy of each of the  $e$  orbital is  $-6 D_q$  and the energy of each of the  $t_2$  orbital is  $4 D_q$ .

(i) For a  $d^1$  system:

The electronic configuration is  $e^1$

$$CFSE = 1 \times (-0.6 D_q) = -6 D_q$$

(ii) For  $d^2$  system:

The electronic configuration is  $e^2$

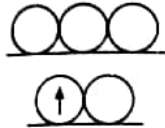
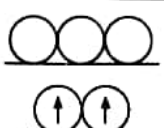
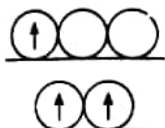
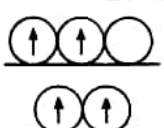
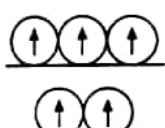
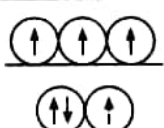
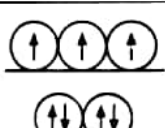
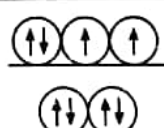
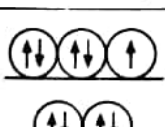
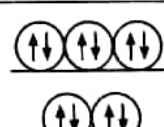
$$CFSE = 2 \times (-6 D_q) = -12 D_q$$

(iii) For  $d^3$  system:

The electronic configuration is  $e^2 t_2^1$

$$CFSE = 2 \times (-6 D_q) + 1 \times 4 D_q = -8 D_q$$

**Crystal field stabilization energies for tetrahedral complexes with metal ions for different  $d^n$**

|                                                                                                            |                                                                                                             |
|------------------------------------------------------------------------------------------------------------|-------------------------------------------------------------------------------------------------------------|
| $d^1$  CFSE = $-6 D_q$  | $d^2$  CFSE = $-12 D_q$ |
| $d^3$  CFSE = $-8 D_q$  | $d^4$  CFSE = $-4 D_q$  |
| $d^5$  CFSE = 0         | $d^6$  CFSE = $-6 D_q$  |
| $d^7$  CFSE = $-12 D_q$ | $d^8$  CFSE = $-8 D_q$  |
| $d^9$  CFSE = $-4 D_q$  | $d^{10}$  CFSE = 0      |

## Spectrochemical Series:

The magnitude of  $\Delta$  varies from strong to weak ligands. Strong ligands are those which exert a strong field on the central metal ion and hence have higher splitting power consequently weak ligands have relatively lower splitting power. Thus strong ligands (e.g.  $\text{CN}^-$ ) give larger value of  $\Delta$  and weak ligands (e.g.  $\text{F}^-$ ) yield a smaller value of  $\Delta$ .

Based on similar data of the absorption spectra for a wide variety of complexes, it is possible to list ligands in order of increasing field strength in a spectrochemical series.

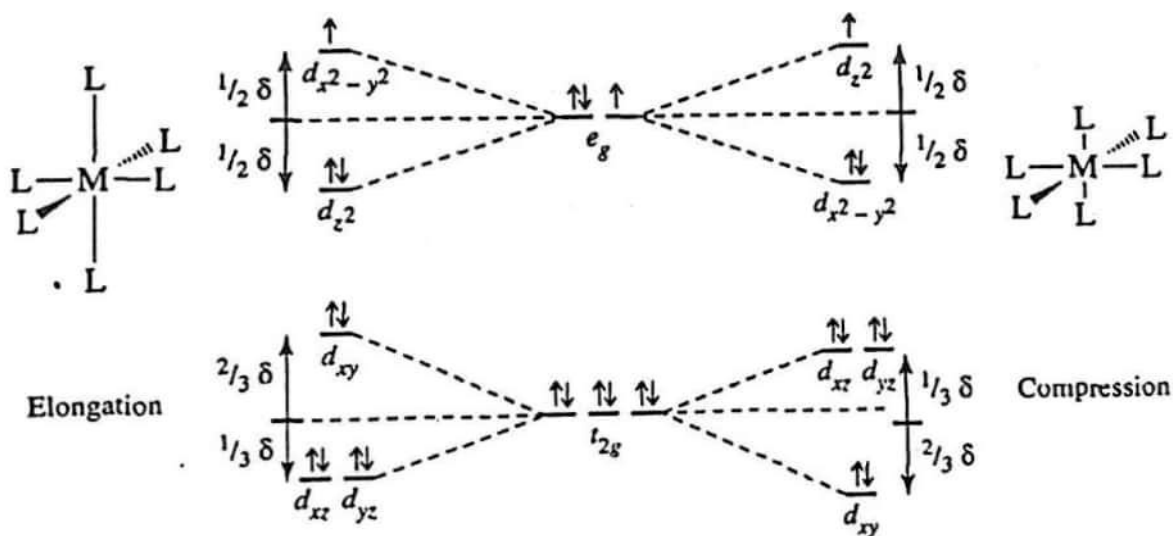
The common ligands can be arranged in the order of their increasing splitting power to cause d-splitting. This series called **spectrochemical series**.

$\text{I}^- < \text{Br}^- < \text{S}^{2-} < \text{Cl}^- < \text{SCN}^- < \text{Cl}^- < \text{N}_3^- < \text{F}^- < \text{OH}^- < \text{C}_2\text{O}_4^{2-} < \text{H}_2\text{O} < \text{NCS}^- < \text{CH}_3\text{CN} < \text{py (pyridine)} < \text{NH}_3 < \text{en}$   
(ethylenediamine) < bipy (2,2'-bipyridine) <  $\text{NO}_2^- < \text{PPh}_3 < \text{CN}^- < \text{CO}$

This series shows that the value of  $\Delta$  in the series also increases from left to right.

## Jahn-Teller Effect

The Jahn-Teller theorem states that **there cannot be unequal occupation of orbitals with identical energies. To avoid such unequal occupation, the molecule distorts so that these orbitals are no longer degenerate.** For example, octahedral  $\text{Cu(II)}$ , a  $d^9$  ion, would have three electrons in the two  $e_g$  levels without the Jahn-Teller effect, as in the center of the Figure below. The Jahn-Teller effect requires that the shape of the complex change slightly, resulting in a change in the energies of the orbitals. The resulting distortion is most often an **elongation along one axis**, but **compression along one axis** is also possible.



In octahedral complexes, where the  $e_g$  orbitals are directed towards the ligands, distortion of the complex has a larger effect on these energy levels and a smaller effect when the  $t_{2g}$  orbitals are involved.

Examples of significant Jahn-Teller are found in complexes :

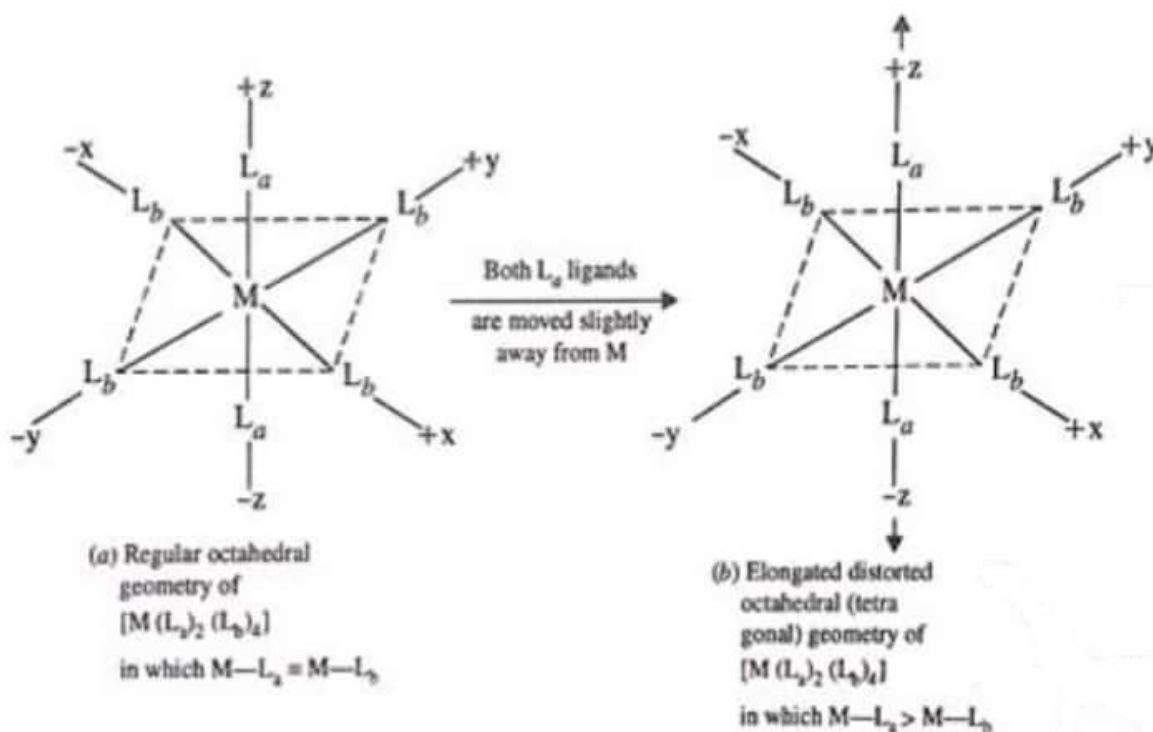
$d^4$  high spin (weak ligands) Cr(II) and Mn(III)

$d^7$  low spin (strong ligands) Co(II) and Ni(III)

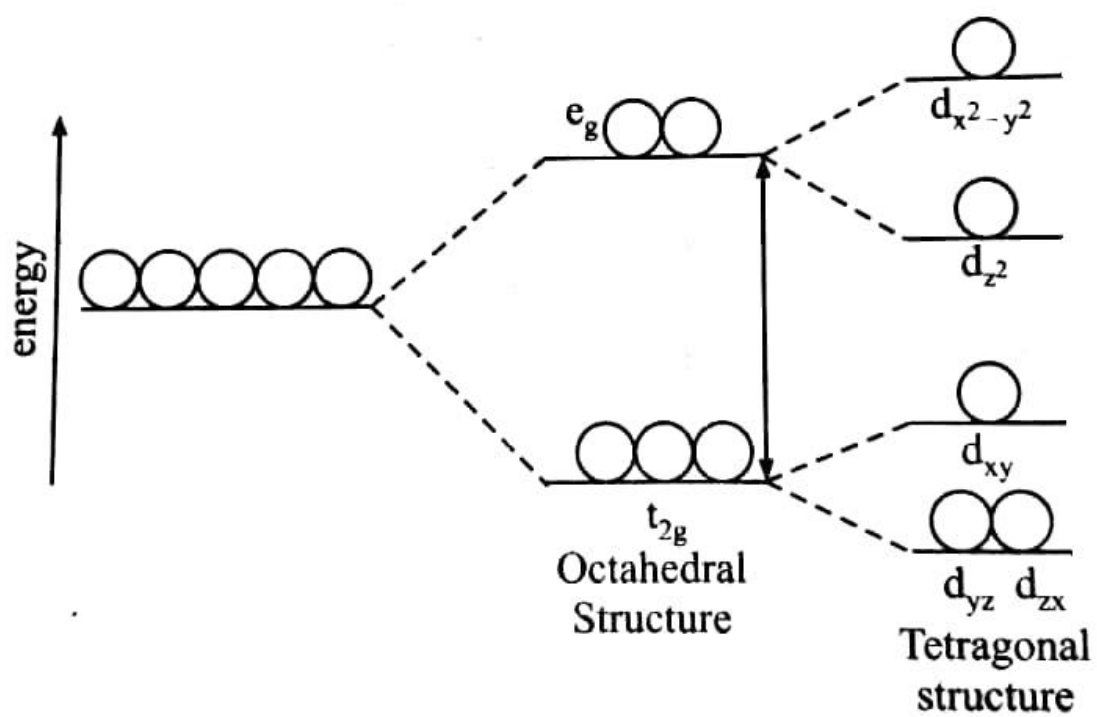
$d^9$  (strong or weak ligands) Cu(II) and Ag(II)

#### Tetragonal distortion of Octahedral geometry:

If two trans ligands in an octahedral  $ML_6$  complex (for example those along the z axis) are moved either towards or away from the metal ion, the resulting complex is said to be tetragonally distorted. Such a distortion is favored because of Jahn-Teller effect.



The figure below illustrates the effect of z-axis stretching on the  $e_g$  and  $t_{2g}$  orbitals in an octahedral complex. Orbitals having a z component (the  $d_{z^2}$ ,  $d_{xz}$  and  $d_{yz}$ ) will experience a decrease in electrostatic repulsion from the ligands and will therefore be stabilized. At the same time, the “non-z” orbitals will be raised in energy, with the barycenter remaining constant. The overall result is that the  $e_g$  level is split into two levels, an upper ( $d_{x^2-y^2}$ ) and a lower ( $d_{z^2}$ ) and the  $t_{2g}$  set is split into ( $d_{xy}$ ) and a doubly degenerate ( $d_{xz}$ ,  $d_{yz}$ ).



Crystal field splitting in octahedral and tetragonal complexes